Structure of near-electrode dissociation-recombination layers under DC stress

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Abstract. The paper deals with processes of current passage through motionless low-conducting liquid in plane-plane electrode system at the injection and dissociation mechanisms of charge formation. The feature of the study is the joint consideration of an approximate analytical solution and the computer simulation. The latter is carried out in dimensionless form, which increases the generality of the results. The analysis of the structure of near-electrode layers in the transient regime and at various ratios between the injection and dissociation mechanisms of charge formation was performed.

1. Introduction

Near-electrode layers emerge in low-conducting liquids due to disbalance between the dissociation and recombination processes and play an important role in the electric current passage through a cell. Though the issue has a long history of investigation, it is still a topical one and is regularly discussed at the present-day conferences (e.g., [1]). The layers affect the measurements of electrophysical properties of a liquid at low voltage especially when ion mobility is determined by the analysis of polarization or depolarization currents. The corresponding currents are rather complicated, and insufficient understanding of their features can lead to incorrect interpretation of the experimental data [2]. Moreover, the presence of near-electrode layers tells on the electrohydrodynamic flow emerging in a cell under the action of a strong electric field [3]. Nevertheless, there are a lot of papers (e.g., [4, 5]) where computations or discussion of the corresponding processes are carried out disregarding the conduction processes.

2. Mathematical model and analytical description

Consider near-electrode dissociation-recombination layers in the plane-plane electrode system with an account of migration and diffusion mechanisms of ion transport and injection and dissociation mechanisms of charge formation. It should be noted that electric double layers [2] that are also located near electrode surfaces are ignored in the paper, since they demand a separate consideration and have minor effect on the processes in the bulk of a low-conducting liquid.

The current passage processes in motionless liquid dielectrics are described by coupled Poisson and Nernst–Planck equations. Consider a 1D problem statement and make the following assumptions: there are only two ion species in the liquid and they are assumed to be monovalent; diffusion coefficient and ion mobility are assumed to be the same for species of both polarities; the intensity of

the dissociation charge formation is independent of the electric field strength; at last, the degree of dissociation is low. In the case, the set of equations can be written in the following dimensionless form:

$$d^2\varphi/dx^2 = -(n_+ - n_-)\, P_0/2 \quad (1)$$

$$\partial n_\pm/\partial t + \partial j_\pm/\partial x = P_0\,(1 - n_+ n_-) \quad (2)$$

$$j_\pm = -\,(\pm n_\pm\, d\varphi/dx) - P_D\, \partial n_\pm/\partial x \quad (3)$$

where φ is the electric potential, n is the ion concentration, j is the density of ion flux, t is the time, x is the coordinate; P_0 and P_D are dimensionless parameters: $P_0 = \sigma_0 L^2 / bV_0\varepsilon\varepsilon_0$, $P_D = D / bV_0$, where σ_0 is the low-voltage conductivity, ε is the relative electric permittivity, ε_0 is the electric constant, L is the length of the interelectrode gap (IEG), V_0 is the voltage across IEG.

All dimensional variables were made dimensionless using their specific values—the length of IEG, the voltage across the gap, and the equilibrium ion concentration ($n_0 = \sigma_0 / 2eb$, where e is the elementary electric charge). The time span during which an ion crosses the IEG ($\tau = L^2/bV_0$) was used as the specific time scale. Chosen to be used as the specific value of the current density j_0 was its migration component: $n_0 bV_0 / L$. The following boundary conditions were utilized: $x \in [0,1]$, $\varphi(0) = 1$, $\varphi(1) = 0$, $j_+(0) = k_+$, $j_-(0) = k_-$, where $k_\pm$ is the dimensionless injection current density at the boundary ($k_\pm = j_{inj,\pm}/j_0$).

According to equation (2), P_0 parameter describes the role of dissociation-recombination processes in the bulk. If P_0 has high values, the volume charge formation plays an important role, which leads to rapid establishment of the steady-state distributions in the most part of IEG. Thus, the perturbation of the concentrations caused by the boundary conditions (e.g., by the absence of the injection charge formation at electrodes) vanishes quickly and fails to penetrate deep into the gap. This corresponds to the case of small length of non-equilibrium near-electrode layers in comparison with the length of the IEG. P_D parameter presents the ratio between the diffusion and migration current density components and appears to be low for liquid dielectrics.

The analytical solution for the set of equations (1)–(3) can be obtained under the following assumptions. Firstly, exclude from the consideration the diffusion current density and the effect of the space charge on the electric field distribution. Secondly, assume the length of the charged layer to be many times less that of the IEG. Thirdly, consider only the steady-state solution. At last, assume the absence of the injection, i.e. $k_\pm = 0$. However, the latter is not a necessary condition and the analytical solution can also be found at $k_\pm \in [0,1]$. As a result, the considered set of equations will possess the following solution for the positive ion concentration:

$$n_+ = 1 - 1 / (1 + xP_0). \quad (4)$$

Equation (4) shows the value P_0 to describe the ratio of the IEG length to that of the non-equilibrium layer. Besides, parameter P_0 designates the degree of the effect of space charge on the external electric field, according to equation (1). This all means that as soon as the volume charge formation assumes the major role the case of the strong effect of the space charge on the electric field realizes instantaneously.

3. Numerical simulation

Proceed with considering the results of numerical calculations by equations (1)–(3). The computations used software package COMSOL Multiphysics basing on the finite element method. To avoid poor numerical convergence during the transient regime, the original 1D problem was transformed into the 2D one, where the second coordinate corresponds to the time. A similar approach is of frequent use in the problem of shock wave propagation.

Examples of steady-state distributions of ion concentrations are presented in figure 1, where three cases are plotted: analytical solution and numerical ones in the simplified (i.e., with disregarding the effect of space charge density on the electric field strength) and complete approaches. The simplified case was considered in the simulation specially for comparison with the analytical solution, since they

both was obtained under nearly the same assumptions. Both plots in figure 1 present only the left half of the IEG. The analytical and simplified solutions are close to each other and differ from the results of the exact computation. The main cause of the corresponding discrepancy is the ignoring the change of the electric field distribution under the effect of space charge density localized in the near-electrode layers. However, the specific length of the layers is described in a correct way in all above cases.

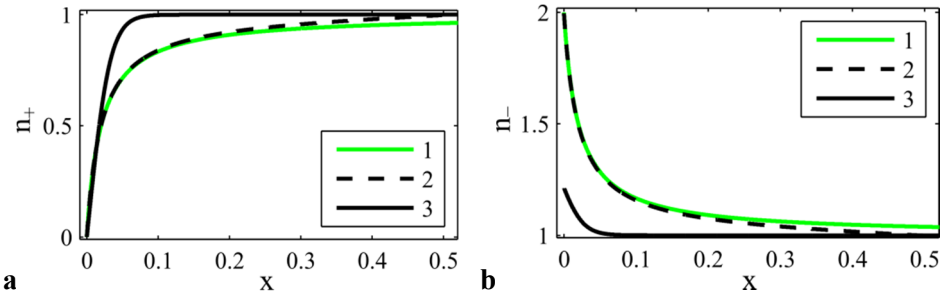

Figure 1. Distributions of dimensionless concentrations of positive (a) and negative (b) ions at $P_0 = 50$: 1—the analytical solution, 2—the simplified and 3—exact solutions.

Briefly analyze the numerical solution. The migration ionic flow provided by the conductivity emerges in the cell when the voltage is applied. However, both the concentration and current density of positive ions is zero at the surface of the positive electrode, since the latter presents itself a "wall" where there is no surface charge forms. Thus, a region of ion deficit arises near the electrode, which is clearly seen in figure 1a. Inside the deficit region, the ion concentration grows from zero level up to its equilibrium value owing to dissociation charge formation. The specific length of the layer is determined by the ratio between the intensity of dissociation charge formation and the migration current density or, according to the analytical solution, by dimensionless parameter P_0.

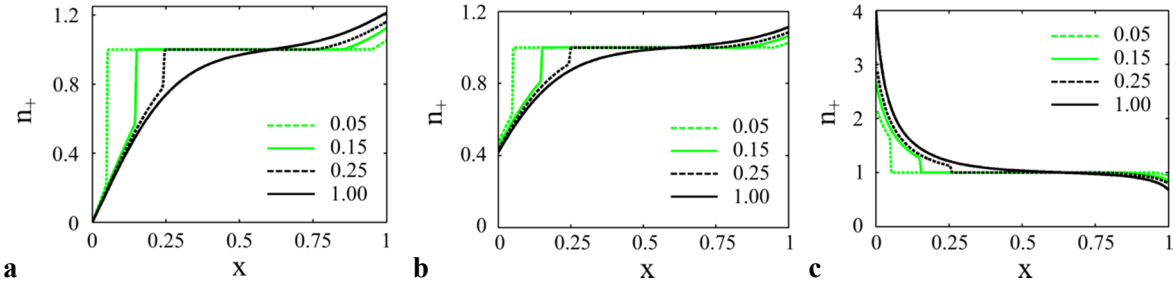

Figure 2. Distributions of dimensionless concentrations of positive ions during the transient regime (with the dimensionless time being specified in the legend) at $P_0 = 5$ for different injection currents: $k_{\pm} = 0$ (a), 0.5 (b) and 2 (c).

Basing on the computation results, consider how the injection charge formation affects the structure of the near-electrode layers (figure 2). When $0 < k_{\pm} < 1$ (figure 2b), the injected ions cause a rise in ion concentration at the boundary comparing to the case without injection (figure 2a); however, the value of the total space charge remains below zero. Emergence of a homocharge takes place only if the injection current prevails over the migration one (i.e., at $k_{\pm} > 1$); however, ion concentration quickly decreases when ions propagate inside the IEG due to strong recombination (figure 2c), with the length of the layer being nearly the same as that in the case without the injection.

Ion distributions presented above were calculated at $P_0 = 5$, which corresponds to the case of the strong effect of the space charge on the electric field strength (figure 3a). Thus, the strength in near-electrode area increased by 40% due to the presence of heterocharge layer at $k_{\pm} = 0$, while reduced by near 50% under the effect of homocharge at $k_{\pm} = 2$.

Lastly, consider the charging current or the so-called current-time characteristic of the transient regime taking place after the pulsed application of the voltage. The computation technique of charging current in the unsteady-state regime is described in [6]. The current starts at the same dimensionless

value—2, which corresponds the classical conduction current provided by initial (equilibrium) ion concentration. Then, however, the current either decreases due to the formation of areas with ion deficit or increases due to the emergence of additional (injected) charge. Besides, it is worth noting that despite quite high injection current density (that is twice the conduction one), the total current increases only by 15%. The latter can be explained by important role of the recombination processes.

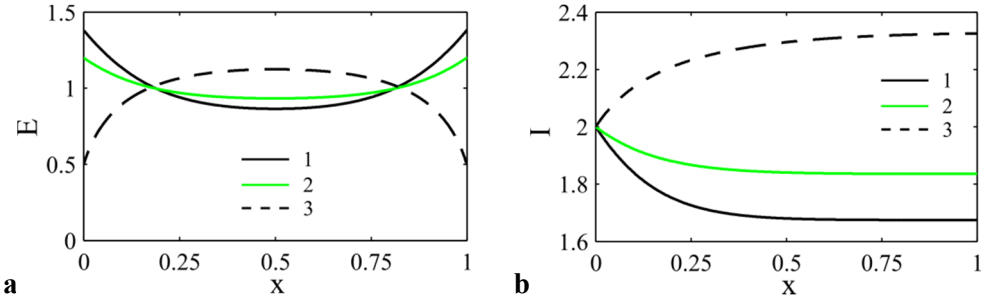

Figure 3. Steady-state distributions of the electric field strength (a) and charging currents (b) at $P_0 = 5$ for different injection currents: 1—$k_{\pm} = 0$, 2—$k_{\pm} = 0.5$ and 3—$k_{\pm} = 2$.

4. Conclusions

The joint consideration of the analytical solution along with the conduction of numerical calculations in dimensionless form allows formulating the following conclusions.

First of all, the degree of the electric field screening by the space charge emerged in the bulk is determined by the same dimensionless parameter P_0 as the degree of the effect of dissociation-recombination processes on the current passage in a low-conducting liquid.

Secondly, the injected ions fail to penetrate inside the bulk when parameter $k_{\pm} < 1$; thus, the homocharge layer is absent in the case. When $k_{\pm} > 1$, the homocharge penetrates into the bulk in the efficient way only at low values of parameter P_0; otherwise (at $P_0 > 1$), the injected charge rapidly recombines during its propagation deep into the gap, with the specific length of penetration being approximately equal to $1/P_0$. This all, in turn, signifies that the consideration of the ion transport and, in particular, electrohydrodynamic flows disregarding the dissociation-recombination processes in the corresponding range of liquids and voltage values (when $P_0 > 1$) is highly ungrounded. Thus, for example, the pure injection model of charge formation fails to describe the structure of electrohydrodynamic flows for liquids with enhanced conductivity or lessened ion mobility.

Thirdly, layers with reduced effective conductivity form near surfaces of both electrodes when the injection is absent, which expresses in the decay of the integral electric current passing through the cell. Accordingly, to obtain correct results, measurements of the low-voltage conductivity of liquid dielectrics are to be made only when the experimental conditions satisfy the following: $P_0 >> 1$.

Acknowledgments

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